Dilute Surfactant Methods for Carbonate Formations

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Disclaimer

Abstract

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally fractured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope, yet it was developed for sandstone reservoirs in the past. The goal of this research is to evaluate dilute (hence relatively inexpensive) surfactant methods for carbonate formations and identify conditions under which they can be effective. Anionic surfactants (Alfoterra 35, 38) recover more than 40% of the oil in about 50 days by imbibition driven by wettability alteration in the core-scale. Anionic surfactant, Alfoterra-68, recovers about 28% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Residual oil saturation showed little capillary number dependence between 10^{-5} and 10^{-2}. Wettability alteration imcreases as the number of ethoxy groups increases in ethoxy sulfate surfactants. Plans for the next quarter include conducting mobilization, and imbibition studies.

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Executive Summary

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally fractured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope, yet it was developed for sandstone reservoirs in the past. The goal of this research is to evaluate dilute (hence relatively inexpensive) surfactant methods for carbonate formations and identify conditions under which they can be effective. Anionic surfactants (Alfoterra 35, 38) recover more than 40% of the oil in about 50 days by imbibition driven by wettability alteration in the core-scale. Anionic surfactant, Alfoterra-68, recovers about 28% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Residual oil saturation showed little capillary number dependence between 10^{-5} and 10^{-2}. Wettability alteration imcreases as the number of ethoxy groups increases in ethoxy sulfate surfactants. Plans for the next quarter include conducting mobilization, and imbibition studies.

Introduction

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally factured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope (Spinler et al., 2000), yet it was developed for sandstone reservoirs in the past (Bragg et al., 1982).

The goal of this research is to evaluate dilute surfactant methods for carbonate formations and identify conditions under which they can be effective. Adsorption, phase behavior, wettability alteration, IFT gradient driven imbibition, blob mobilization at high capillary and Bond numbers will be quantified. An existing laboratory simulator will be modified to incorporate the mechanisms of surfactant transport and effective parameters will be developed to model this process in a dual porosity reservoir simulator. Field-scale simulations will be conducted to identify criteria under which dilute surfactant methods are feasible without active mobility control.

This report summarizes our results for the period of January, 2004 through March, 2004. The five tasks for the project are: (1) Adsorption, (2) Wettability alteration, (3) Gravity and viscous mobilization, (4) Imbibition, and (5) Simulation. The third and fourth tasks were worked on this quarter. The results of imbibition, viscous mobilization, and wettability of four additional surfactants are highlighted in this report.

Experimental

Material

Imbibition studies were conducted with three surfactants: Alfoterra 35, 38 and 68. Our studies (described in previous reports) show that Alfoterra 35 and 38 are good wettability altering agents. Alfoterra 68 lowers the IFT considerably. Four ethoxy sulfates: CS-130, C-230, B-330S and B-27 were also used for phase behavior and wettability studies. Surfactants were used as supplied.

Calcite (Iceland spar) were supplied by Scientific Ward. The oil was from a West Texas fractured carbonate field (supplied by Marathon Oil Company). It was 28.2 °API, 19.1 cp viscosity, 0.2 acid number and 1.17 base number. It was similar to the oil MY3 used by Hirasaki and Zhang (2003). Synthetic brine composed of Na_2CO_3 was used for the anionic surfactants to lower adsorption and surfactant requirement.

Imbibition Study

Outcrop limestone 1.5 inch diameter and 6 inch long cores were used. Air permeability of these cores were about 120 md. Porosity was 22.5%. Each core was first completely saturated with a 0.1 N NaCl brine. 5 PV of crude oil was injected to drive the core to connate water saturation. Oil saturation at the end of this oil flood was 72%. The core was immersed in the crude oil and aged for 18 days at 80 °C. The imbibition cell was filled with the surfactant-Na2CO3 solution. The aged core was placed in an imbibition cell and the oil production was monitored.

Capillary Number Study

For obtaining capillary desaturation curve, following procedure was followed. Surfactant (Alfoterra 38, 0.05 wt% in 0.3 M Na_2CO_3) was equilibrated with crude oil in 1:1 ratio for a period of 2 days, with gentle mixing. The equilibrated solutions were used as the aqueous and oil phase for the capillary number curve. The IFT between the two was obtained as 10^{-2} dynes/cm. The contact angle on calcite was observed as 33^{o}, essentially rendering the calcite surface water-wet. The core used for this study had a porosity of 22.5 % and permeability of 120 md. The core was vacuum dried and then flooded with equilibrated surfactant brine to obtain 100% aqueous saturation. The equilibrated oil was injected into this core and a final oil saturation of 80 % was obtained. The capillary number dependence was studied by flooding this core with equilibrated surfactant solution at various flow rates and calculating the residual oil saturation by material balance.

Phase Behavior Study

Dilute solutions of anionic surfactants (0.05 active wt%) were prepared with varying concentrations of sodium carbonate (Na_2CO_3). These solutions were equilibrated with equal volumes of oil on a tube shaker for a period of two days. Thereafter the tubes were removed and left to settle for a day. The number of phases and the color of the phases were observed, which indicated the shift from Winsor type II- to type II+ phase behavior with the increase in salinity of the solution.

Interfacial Tension Measurement

The IFT between the equilibrated brine and oil phases was measured with help of a spinning drop tensiometer. The equilibrated brine solutions and the equilibrated oil from the phase behavior study were used to determine the interfacial tension between the synthetic brine and oil. This led to the identification of the region of lowest interfacial tension or optimum salinity of the given system. The subsequent wettability experiments were performed at the optimum salinity obtained from these measurements.

Wettability Test

The wettability tests were done on mineral plates (2 cm x 1 cm x 0.2 cm). The plates were polished on a 600 mesh diamond lap and equilibrated with synthetic brine for a day. The initial wettability state of the plate was determined by measuring the advancing and recently receded contact angle of oil with the plate immersed in brine. The plate was removed from brine and aged with oil at an elevated temperature (~80 °C) in the oven for about two days to make it oil-wet. The reservoir temperature is close to the room temperature (~30 °C), but the elevated temperature aging is done to compensate for the short aging time (compared with the geological time). After removing from the oven, the plate (with oil stuck around it) was contacted with synthetic (sodium carbonate) brine for an hour and the advancing contact angle was measured. The contact angle measurements were made with the help of a Kruss goniometer. Thereafter, the synthetic brine was replaced by the surfactant-brine solution and the evolution of contact angle was studied for a period of two days by imaging the drops attached to the plate. In the cases where the drops were too small (<<0.1 mm), it was difficult to measure an accurate contact angle and a post-wettability test was performed. In the post-wettability test, the plate was washed with brine following the surfactant treatment. This plate was then placed in the brine solution and an oil drop was deposited on the bottom of the surface with the help of an inverted needle (oil drops did not attach to the top of the plate in these cases). The contact angle was then measured. This gave the final wettability state of the plate. Drops were deposited on several parts of the plate and the range of the contact angles was noted.

Results and Discussion

Imbibition

To test the wettability of a core aged in the crude oil for 18 days, a drop of water was placed on the top of the core. Figure 1 shows the picture of the drop. It is not spontaneously imbibed into the core. That shows that the core is not water-wet. Four such aged cores were used for the imbibition study. The initial water saturation was ~27.5% in each of these cores. Each imbibition cell had a different brine. Cell 1 had 0.05 wt% Alfoterra 35 and 0.3 M Na2CO3 brine. Cell 2 had 0.05 wt% Alfoterra 38 and 0.3 M Na2CO3 brine. Cell 3 had 0.05 wt% Alfoterra 68 and 0.3 M Na2CO3 brine. Cell 4 had 0.1 M NaCl brine.

Figure 1. A drop of brine on top of a limestone core aged in crude oil

The oil production in each cell due to spontaneous imbibition is shown in Figure 2. The spontaneous imbibition volumes in cells 1 and 2 are about the same and higher than the other two. About 40% of the oil has been produced in about 50 days of spontaneous imbibition with

Alfoterra 35 and 38. These two surfactants were good wettability altering agents in the calcite plate wettability study. The production in cell 3 is about 28% in 50 days. Alfoterra 68 induces spontaneous imbibition, but to a lower extent compared to the first two cases. There was very little imbibition in cell 4. This indicates that the core is oil-wet.

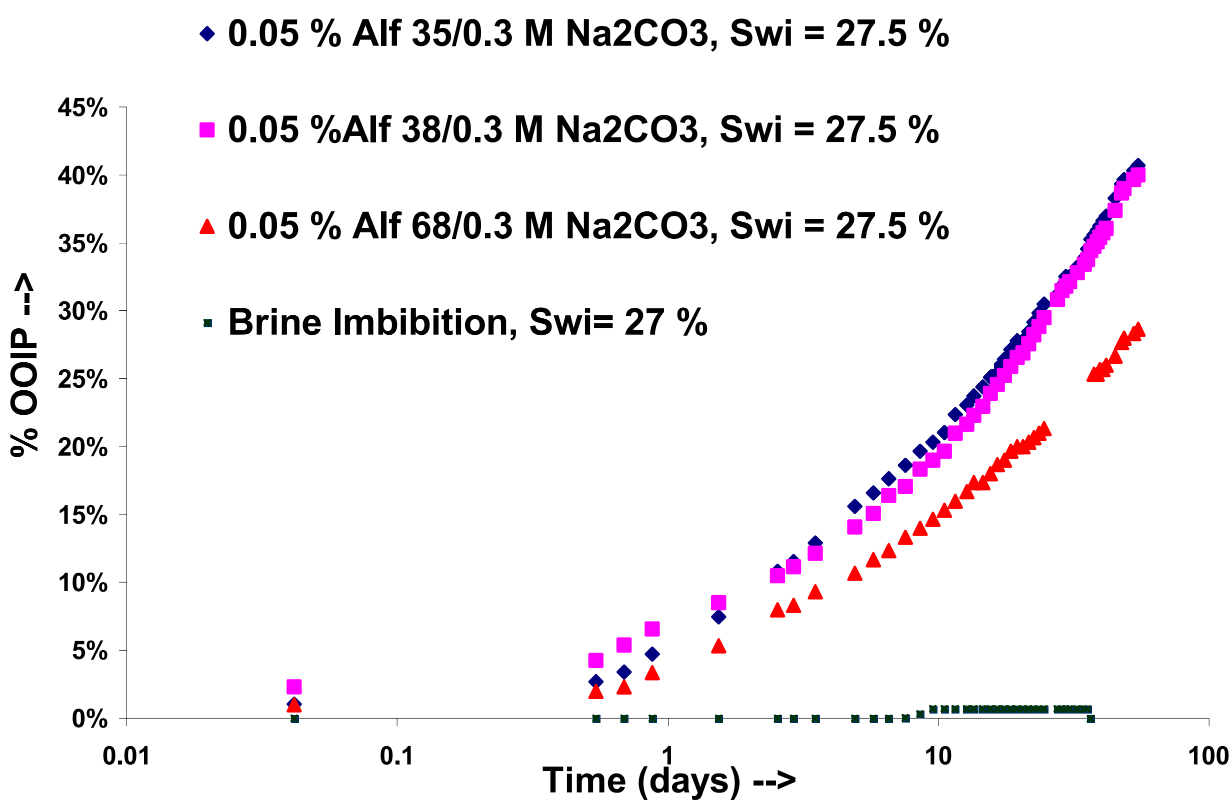

Figure 2. Spontaneous imbibition of different brines into oil-wet limestone core with Swi=27.5%

The imbibition obtained with these surfactants can be compared to literature values. Austad & Standness (2003) obtained about 15% OOIP recovery at 40 C and about 45% OOIP recovery at 70 C from spontaneous imbibition with 1 wt% DTAB for chalks with Swi=26%. Xie et al. (2004) have used nonionic surfactants to enhance oil recovery from dolomitic Class II reservoirs.

They observed about 5-10% recovery. This indicates that the anionic surfactants have performed well in the laboratory-scale.

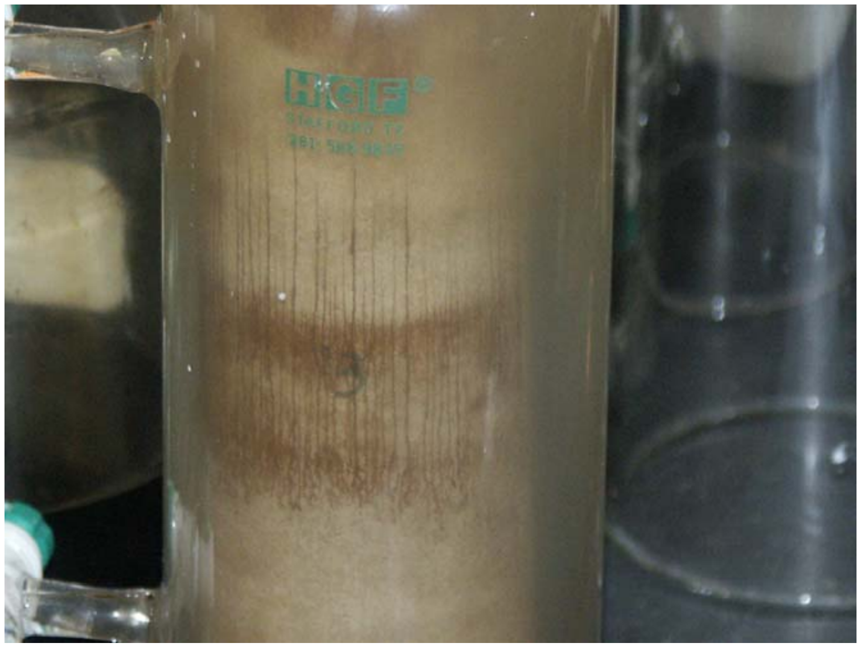

Figure 3. View of the core in imbibition cell 1 with Alfoterra 35

Figure 4. View of the core in imbibition cell 3 with Alfoterra 68

Figure 3 shows the core in Cell 1 during imbibition. Oil was observed to leave from the sides of the core, i.e., with Alfoterra 35. The fluid on top of the core in Cell 1 was turbid. Therefore, we could not determine whether oil was leaving from the top or not. Oil production from the side is an indication that the imbibition process is driven partly by wettability alteration. Figure 4 shows the core in Cell 3 during imbibition with Alfoterra 68. Oil was observed to leave from the top of the core. Oil production from the top is an indication of gravity-driven, low-tension imbibition.

Capillary Number Dependence

The capillary number is defined as $N_c = V\mu / \gamma$, where μ is viscosity of the displacing fluid, γ is the interfacial tension between the two fluids and V is the superficial fluid velocity. Values of V were chosen such that N_c varied from 10^{-5} to 10^{-2}. The residual oil phase saturation is plotted in Figure 5 as a function of the capillary number. At $N_c = 10^{-5}$ oil saturation is reduced to 36% from the original saturation of 80%. But with increase of N_c varied from 10^{-5} to 10^{-2}, the Sor does not decrease much (only ~6%). We are conducting additional experiments to understand this behavior.

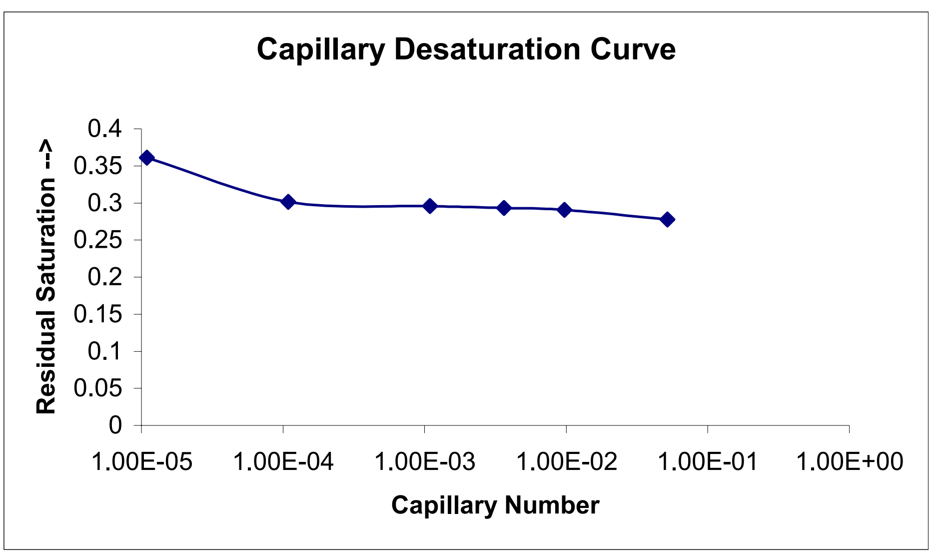

Figure 5. Capillary desaturation curve

Phase Behavior

Figure 6 shows the phase behavior of crude oil - brine (Na_2CO_3) - surfactant system for a typical case (CS-230). Water-oil ratio is kept at 1:1 in all cases shown. The concentration of the surfactant is kept constant at 0.05 wt% and the Na_2CO_3 concentration is increased from 0 to 1.8 M. As the caustic concentration increases, the darkness of the aqueous phase increases, reaches a maximum and then decreases. In this case, the aqueous phase is observed to be the darkest at a Na_2CO_3 concentration of 1 M. An optimal salinity is defined in the next section on the basis of the lowest water-oil interfacial tension; 1 M salinity is close to the optimal. A small, middle phase microemulsion is also observed in the near-optimal region. The aqueous phase becomes clear at the Na_2CO_3 concentration of 1.4 M indicating Winsor type II+ microemulsion. At this point, the system is in the over-optimum salinity regime.

0.0M 0.1M 0.2M 0.4M 0.6M 0.8M 1.0M 1.2M 1.4M 1.8M

Figure 6. Salinity scan with Na2CO3, 0.05% CS-230

Interfacial Tension

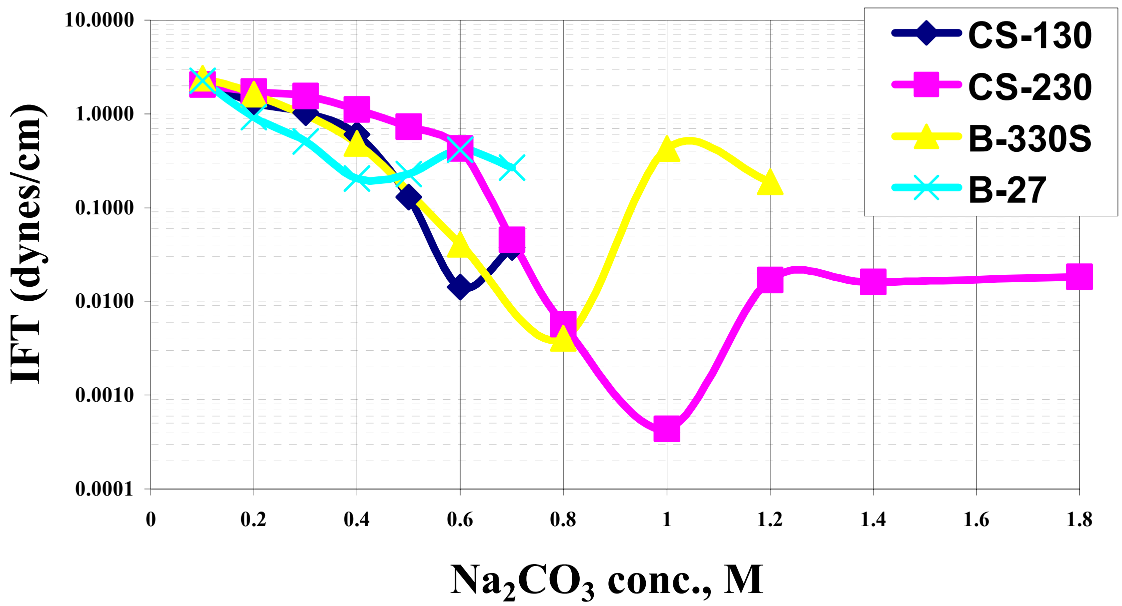

Figure 7. IFT between the oil and brine phases at varying Na2CO3 concentrations

Figure 7 shows the interfacial tension (IFT) between the aqueous and the oleic phases as a function of Na_2CO_3 concentration in these crude oil - brine (Na_2CO_3) - surfactant systems. Water-oil ratio is again kept at 1:1 in all cases shown. The anionic surfactant concentration is also kept constant at 0.05 wt%.

The overall trend is similar for all the surfactants, i.e., the IFT decreases with increasing Na_2CO_3 concentration before reaching a minimum and then increases. The optimal salinity changes from 0.4 to 1 M Na_2CO_3 for the four surfactants. The minimum IFT is 10^{-2} mN/m for CS-130, $6x10^{-4}$ mN/m for CS-230, $5x10^{-3}$ mN/m for B-330S, and $2x10^{-1}$ mN/m for B-27. As the number of ethoxy group increases, the minimum tension decreases and then increases. The lowest IFT is observed for CS-230.

Wettability

Wettability was evaluated by measuring water-oil contact angles. All the contact angle measurements for the anionic surfactants were made at a surfactant concentration of 0.05 active wt%, at the optimum salinity obtained from the IFT experiments. Before aging with oil, the mineral plate is found to be intermediate-wet with advancing contact angle greater than 90° and receding contact angle less than 90°. After aging the calcite plate with the crude oil at an elevated temperature for 44 hrs, the mineral plate becomes completely oil-wet with an advancing contact angle close to 160°. The oil-aged plate is immersed in brine and the oil-water contact line on the calcite plate is photographed to obtain this data. The brine is then replaced with a surfactant solution at its optimal salinity. When exposed to the surfactant - brine solution, (much of the oil is released from the plate) the advancing contact angle decreases with time and stabilizes at a value depending on the drop size.

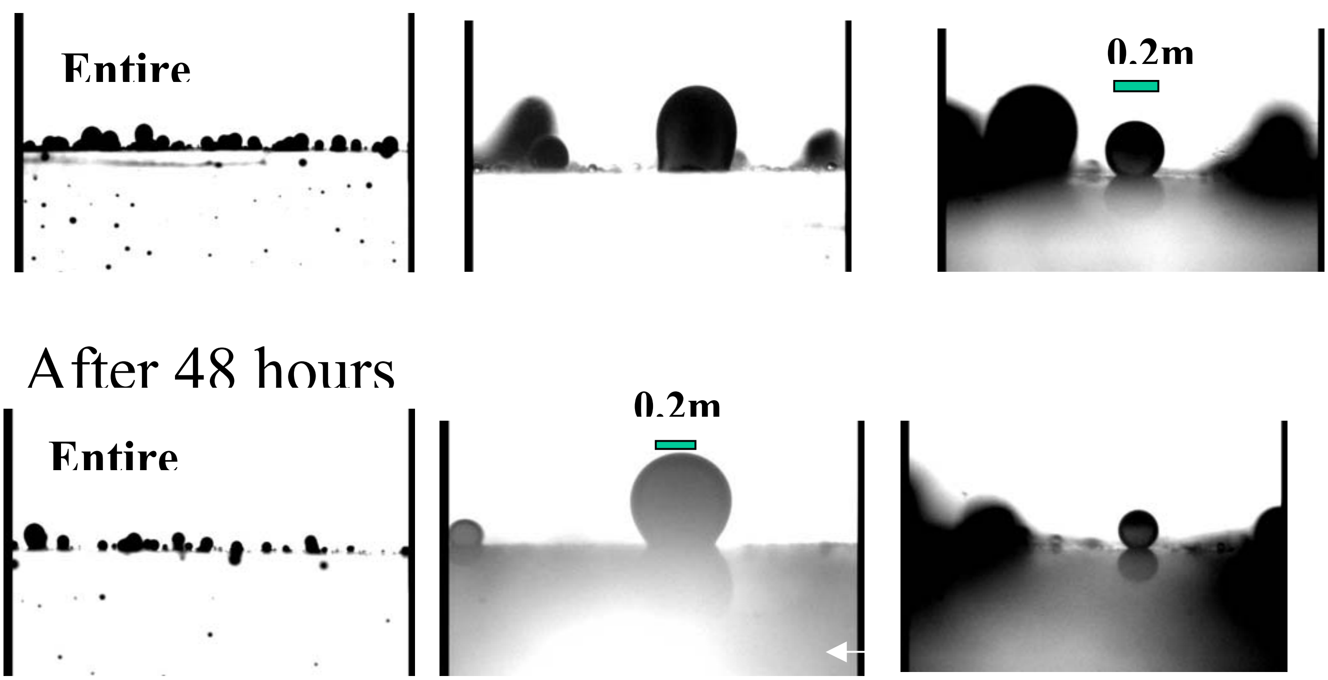

Figure 8. Shapes of oil drop left at the end of the wettability test

Figure 8 shows the calcite plate upper surface at different times after the oil-aged surface was exposed to the surfactant B-330S brine solution. The equilibrium IFT was lower than 10^{-2} mN/m for this surfactant. Oil leaves the surface because of low IFT. After 48 hours, the calcite plate looks water-wet. Figure 9 shows the contact angle at the end of wettability tests (including the post wettability-tests for CS-230 and B-27). As the number of ethoxy groups increase the wettability alteration is higher. CS-230 appears intermediate wet. B-330S and B27 appear water-wet.

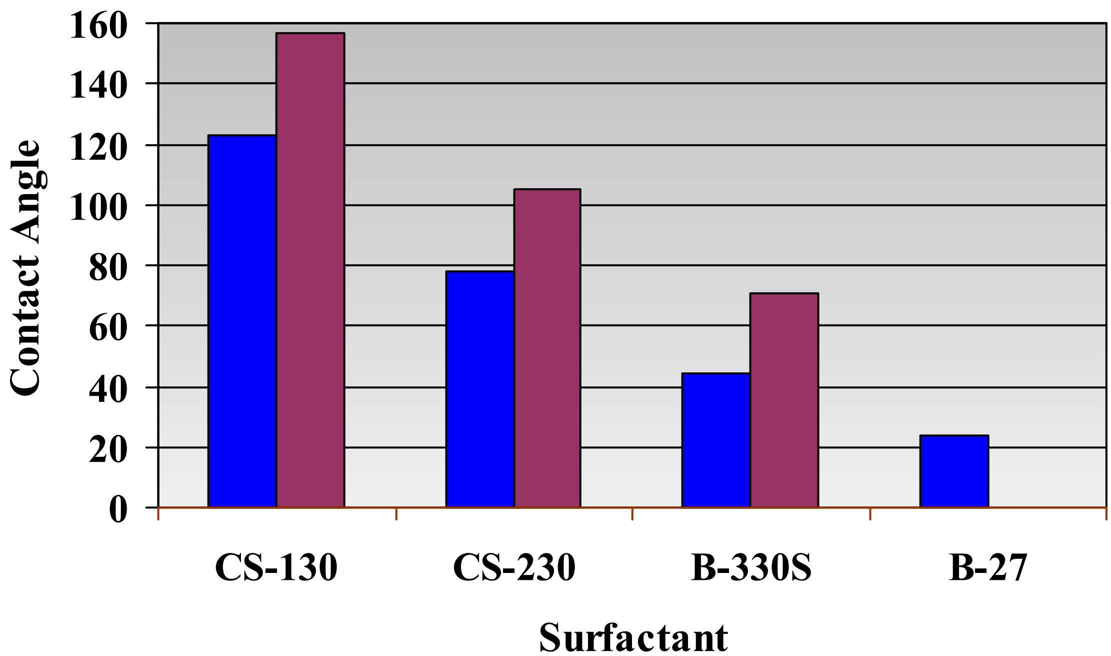

Figure 9. Contact angle at the end of the wettability test

Technology Transfer

Marathon oil company is one of the major producers in West Texas carbonates. We have briefed them about our project plans and have received field samples. We are working with Oil Chem Technology, Stepan and Sasol on surfactants. These collaborations are extremely important to the success of our project. We have written a paper, SPE 89423, which will be presented at the 14^{th} SPE/DOE IOR symposium in Tulsa, April, 2004.

Conclusions

Anionic surfactants (Alfoterra 35, 38) recover more than 40% of the oil in about 50 days by imbibition driven by wettability alteration in the core-scale (Task 4). Anionic surfactant, Alfoterra-68, recovers about 28% of the oil by lower tension aided gravity–driven imbibition in the core-scale (Task 4). Residual oil saturation showed little capillary number dependence between 10^{-5} and 10^{-2} (Task 3). Wettability alteration imcreases as the number of ethoxy groups increases in ethoxy sulfate surfactants (Task 2).

Plans for Next Reporting Period

- Mobilization experiments (Task 3)
- Imbibition experiments (Task 4)

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